

**MORPHOLOGICAL, MECHANICAL AND
THERMAL PROPERTIES OF AMORPHOUS
COPOLYESTER/POLYOXYMETHYLENE BLENDS**

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**MORPHOLOGICAL, MECHANICAL AND THERMAL PROPERTIES OF
AMORPHOUS COPOLYESTER/POLYOXYMETHYLENE BLENDS**

by

LAM KOK LOON

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$\%C_A$	Percentage of A polymer continuity 35
m_a	Mass after extraction 35
m_b	Mass before extraction 35
w	Weight fraction 35
ΔH	Heat of fusion of sample 45
ΔH_f^0	Heat of fusion for 100% crystalline 45
E'	Storage modulus 46
E''	Loss modulus 46
a	Total notch length 47
B	Thickness of the specimen 47
F_{max}	load at crack growth initiation 47
K_c	Fracture toughness 47
W	Width of the specimen 47
S	Initiation stiffness 48
F	Maximum force in the force-deflection trace 48
ΔH_m	Enthalpy of melting 53
ΔT_m	Melting temperature range 53
T_g	Glass transition temperature 53
T_m	Melting temperature 53
ΔH_c	Enthalpy of crystallization 54
ΔT_c	Crystallization temperature range 54
T_c	Crystallization temperature 54
T_s	Tensile at break 58
E_B	Elongation at break 58
E_b	Energy to tensile failure 60

LIST OF ABBREVIATION

ABS	Acrylonitrile-butadiene-styrene
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
EPDM-g-MMA	Ethylene-propylene-diene elastomer grafted with methyl methacrylate
EPM-g-MA	Maleic anhydride grafted ethylene propylene rubber
EPR-g-GMA	Ethylene/propylene rubber grafted with glycidyl methacrylate
EVOH	Ethylene-vinyl alcohol
FTIR	Fourier-transform infrared spectroscopy
HDPE	High density polyethylene
iPP	Isotactic polypropylene
MFI	Melt flow index
MFR	Melt flow rate
PA	Polyamide
PBT	Poly(butylene terephthalate)
PC	Polycarbonate
PE	Polyethylene
PET	Poly(ethylene terephthalate)
PETG	Poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate)
PLLA	Poly(L-lactide)
PMMA	Poly(methyl methacrylate)
POM	Polyoxymethylene
PP	Polypropylene
PPE	Poly(2,6-dimethyl-1,4-phenylene ether)
PPO	Poly(2,6-dimethyl-1,4-phenylene oxide)

PPT	Poly(trimethylene terephthalate)
PS	Polystyrene
PVC	Polyvinylchloride
SAN	Poly(styrene-co-acrylonitrile)
SBS	Styrene–butadiene–styrene
SEBS	Styrene–ethylene/butylene–styrene
SEM	Scanning electron microscopy
sPS	Synodiotactic polystyrene
TPE	Thermoplastic elastomer
TPEg	Maleated thermoplastic elastomer
TPU	Thermoplastic polyurethane
w.r.t.	With respect to

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SIFAT MORFOLOGI, MEKANIK DAN TERMA BAGI GAULAN KOPOLIESTER AMORFUS /POLIOKSIMETILENA

ABSTRAK

Kajian terhadap gaulan kopoliester amorfus/polioksimetilena (POM) yang telah dilaksanakan adalah terdiri daripada dua bahagian yang utama. Kajian bahagian pertama adalah berkaitan dengan kesan komposisi ke atas sifat-sifat morfologi, mekanik dan terma bagi gaulan kopoliester amorfus/POM. Kopoliester yang dipilihkan ialah poli(etilene glikol-ko-sikloheksena-1,4-dimetanol terephthalate) (PETG). Gaulan PETG/POM yang merangkumi keseluruhan siri komposisi telah dihasilkan dengan menggunakan penyebatan leburan. Spesimen gaulan disediakan dengan kaedah pengacuan suntikan dan mampatan. Kebanyakan sifat-sifat bagi gaulan PETG/POM yang tidak serasi ini mematuhi peraturan penambahan sebagai fungsi komposisi, seperti indeks aliran leburan (MFI), ketumpatan, tensil dan kekakuan lenturan. Walaubagaimanapun sifat-sifat seperti pemanjangan pada takat putus, tenaga serapan untuk gagal, kekuatan lenturan, kekuatan hentaman Izod yang ditakukkan dan keliatan rekahan statik, K_c telah menunjukkan nilai yang lebih rendah daripada komponen asas gaulan. Ini disebabkan kelemahan pelekatan antaramuka antara PETG dan POM. Darjah penghabluran bagi gaulan PETG/POM menurun dengan peningkatan kandungan PETG. Ini adalah disebabkan oleh sifat amorfus PETG. Morfologi 'co-continuous' telah ditentukan dengan menggabungkan ekstraksi pilihan dan mikroskopik elektron pengimbasan (SEM) bagi gaulan PETG/POM 60/40 dan 50/50 wt%/wt%. Permukaan rekahan tensil bagi gaulan 50/50 menunjukkan morfologi fibril yang diperoleh oleh pengacuan suntikan yang telah mengubahkan struktur fasa permulaan 'co-continuous'. Pemanjangan pada takat putus, tenaga serapan untuk gagal, kekuatan hentaman Izod yang ditakukkan dan keliatan rekahan statik bagi gaulan 'co-continuous' PETG/POM lebih tinggi daripada gaulan yang mempunyai struktur fasa berserakan. Tetapi nilainya masih rendah daripada PETG dan POM.

Bahagian kedua dalam kajian ini telah melibatkan kajian terhadap penggunaan termoplastik poliuretana (TPU) sebagai bahan serasi dalam gaulan PETG/POM. Dua jenis TPU (iaitu berasaskan poliester dan polieter) telah digunakan dalam sistem gaulan ini. Gaulan 'co-continuous; PETG/POM (50/50 wt%/wt%) telah disediakan. Sifat mekanik bagi gaulan 'co-continuous' PETG/POM telah dikajikan dengan menggunakan ujian lenturan dan 'single edge notch tensile test' (SEN-T). Kekuatan lenturan gaulan PETG/POM telah menurun dengan penambahan TPU. Ini disebabkan oleh TPU yang bersifat elastomer. Kesan penyerasian TPU telah dibuktikan dengan peningkatan dalam keliatan rekahan dan disokongkan oleh pemerhatian SEM. Permukaan rekahan SEN-T bagi gaulan yang ditambah kesan penyerasi menunjukkan lebih banyak alah ricih matriks jika dibandingkan dengan sistem tanpa penambahan bahan penyerasi. Nilai K_c bagi gaulan PETG/POM menurun dengan peningkatan kelajuan ujian. Kesan optimum bagi keliatan rekahan telah didapati dalam gaulan PETG/POM yang telah diserasikan dengan penambahan TPU berasaskan polieter pada takat kelajuan ujian 100mm/min. TPU berasaskan polieter menunjukkan bahan penyerasi yang lebih berkesan kerana jumlah kandungan yang diperlukan adalah 1/2 daripada TPU berasaskan poliester untuk mencapai nilai K_c yang sama. Ini adalah disebabkan oleh sifat elastomer TPU berasaskan poliester. Sifat kelembutan semulajadi bagi TPU berasaskan polieter dapat memberikan kesan keliatan rekahan yang lebih baik daripada TPU berasaskan poliester disebabkan sifat yang lebih keras secara semulajadi.

MORPHOLOGICAL, MECHANICAL AND THERMAL PROPERTIES OF AMORPHOUS COPOLYESTER/POLYOXYMETHYLENE BLENDS

ABSTRACT

The research on amorphous copolyester/polyoxymethylene (POM) blends consists of two parts. The first part was to study the effects of blend composition on the morphological, mechanical and thermal properties of amorphous copolyester/POM blends. Poly(ethylene glycol-co-cyclohexane-1, 4-dimethanol terephthalate) (PETG) was selected as copolyester. PETG/POM blends were produced by melt blending covering the whole composition range. The specimens of the blends were prepared using injection and compression molding. Properties such as melt flow index (MFI), density, tensile and flexural stiffness of these incompatible PETG/POM blends followed the additivity rule as a function of composition. However, the elongation at break, energy absorbed until tensile failure, flexural strength, notched Izod impact strength and static fracture toughness, K_{IC} showed lower values than either of the neat blend components. This was traced to the poor interfacial adhesion between PETG and POM. The degree of crystallinity of the PETG/POM blends decreased with increasing the PETG concentration. This was attributed to the amorphous nature of PETG. A co-continuous morphology was ascertained by the combination of selective extraction and SEM for the blends PETG/POM 60/40 and 50/50 wt%/wt%. The tensile fracture surface of the 50/50 blend exhibited a fibrillar morphology owing to the injection molding-induced distortion of the initial co-continuous phase structure. The elongation at break, energy to tensile failure, notched Izod impact strength and fracture toughness of the co-continuous PETG/POM blends were slightly higher than those blends with dispersed phase structure. However, the values were still below the corresponding values of the neat PETG and POM.

The second part of the research involves the usage of thermoplastic polyurethane (TPU) as a compatibilizer in PETG/POM blends. Two types of TPU (i.e. polyester based and polyether based) were used to compatibilize the blends system. The co-continuous PETG/POM (50/50 wt%/wt%) blends were prepared. The mechanical properties of the co-continuous PETG/POM blends were studied through flexural and single-edge notch tensile test (SEN-T). The flexural strength of the PETG/POM blends was decreased in the presence of TPU. This was attributed to the elastomeric nature of the TPU. The compatibilizing effects of TPU on the PETG/POM blends were proven by moderate improvement in the fracture toughness and confirmed by the SEM observation. The SEN-T fractured surface of the compatibilized blends showed gross matrix shear yielding as compared to the uncompatibilized system. The K_{IC} values of the PETG/POM blends decreased with the increasing of testing speed. The optimum toughening effect was observed in PETG/POM blends compatibilized with polyether based TPU at testing speed of 100mm/min. The polyether based TPU is a more efficient compatibilizer as the amount required being 1/2 to that of the polyester based counterpart to achieve the same K_{IC} value. This was attributed to the elastomeric nature of the polyether based TPU. The softer nature of polyether based TPU could provide better toughening effect than the polyester based TPU, which is relatively harder in nature.

CHAPTER 1 INTRODUCTION

1.1 Introduction

Commodity plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC) make up a large proportion of total tonnage of plastics currently being used mainly for consumer products or non load bearing application. However, there is a high performance plastics also known as engineering plastics, which have been developed to provide the combinations of lightness, good balance of stiffness, toughness and over a wide range of temperature applications. The use of engineering plastic in the areas dominated by the use of metal and ceramics have been growing up day by day. However, an individual engineering plastic frequently, does not meet the requirement of new applications. In order to develop a marketable product, development of new polymer has continued. Nevertheless, the developments of a new polymer need a big amount of investment and have to spend a lot of time. Therefore, many plastics manufacturers are using blending polymers to develop new polymer, which is more economical, convenient and widely accepted. Polymer blending is growing importance today, because the blend can be tailored to meet the requirements of specific applications. In addition, since the properties of blend system are functions of the composition, the blend can be easily and quickly modified to meet performance and cost objectives required by new or changing markets [Mark *et al.*, 1988b].

Nowadays, polymer blends constitute over 30wt% of polymer consumption and the annual growth rate of about 9% in the past 12 year constantly and its continuously increases [Utracki, 1998]. Benefits of blending can be discussed from the perspective of properties and economies it can bring to the manufacturer. To date, blending can be used to gain economy by diluting expensive engineering plastic with commodity ones.

New blend systems are particularly attractive because the research and development costs are low. This allows the blend to be produced at a lower cost [Mark *et al.*, 1988b].

In 20th century, there are about 65% of polymer blends and alloys have being produced by polymer manufacturers, about 25% by compounding companies and other by the transformers. The advantages of the blending technology are listed below [Utracki, 1990]:

- Better processability, so improved product uniformity and scrap reduction.
- Product tailorability to specific customer needs, thus better customer satisfaction.
- Quick formulation changes, so better plant flexibility and high productivity
- Blending reduces the number of grades that need to be manufactured and stored, so savings space and capital investment.
- Recyclability of blends achieved by control of morphology.

Polymer blends are now a major field of research and development activity due to their vast potential in acknowledging today's industrialized societies. There are wide applications of engineering plastics blends in the automotive, appliances, consumer applications and home electronics industry. Improving mechanical properties such as toughness is one of the main reason to develop a novel thermoplastic blends. Polyoxymethylene (POM) is one of the major engineering thermoplastics that have very good mechanical properties, such as tensile strength, flexural modulus, high creep, and good fatigue endurance and deflection temperature. However, POM is notch sensitive materials. Incorporation of an amorphous polymer into POM for toughening purposes has been reported in many studies [Chiang & Huang, 1989; Chang *et al.*, 1991; Erro *et al.*, 1996]. Chiang and Huang [1989] reported on the effects of polyether- and polyester-based thermoplastic polyurethane (TPU) blended with POM. The POM/TPU

blends exhibited good impact strength, high strain and good elastic recovery. The above properties were strongly dependent on the composition ratio, processing conditions and resulting morphology. Chang *et al* [1991] studied the immiscible blends of polycarbonate (PC) and POM. Incorporation of PC into POM significantly increased the modulus and yield strength of the latter. In a more recent study, blends of POM with PP compatibilized with ethylene-vinyl alcohol (EVOH) copolymers were investigated by Huang *et al* [2003].

Poly (ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate) (PETG) is a fully amorphous polymer with high toughness and clarity. Yu and co-worker [2002; 2003] studied the compatibilization and toughening of PETG, PETG/thermoplastic elastomer (TPE) and PETG/ poly(ethylene terephthalate) (PET) with a maleated thermoplastic elastomer. The addition of maleic anhydride grafted TPE into PETG/TPE also improved the dispersion of the TPE in PETG. Papadopoulou and Kalfoglou [1997a; 1997b] investigated the compatibility behavior of blends of PETG with poly(butylene terephthalate) (PBT) and PET over complete composition range. Samios and Kalfoglou [2000] studied the phase behavior and solid-state properties to characterize the compatibility of PETG/bisphenol-A polycarbonate over the complete composition range. Samios and Kalfoglou also [2001] investigated the compatibilization effect of poly(ethylene-co-vinyl alcohol)/PETG blend by using acrylic-modified polyolefin ionomers as compatibilizers. The PETG/EVOH blends could be compatibilized using ethylene-acrylic type ionomers (i.e. sodium and zinc cations).

1.2 Problem statement

POM is a crystalline polymer with a good combination of mechanical properties. It is particularly excellent in fatigue endurance and outstanding in friction/wear properties, chemical resistance, creep resistance, and dimensional stability. Besides that, POM exhibits a low absorption of water. POM is accepted as engineering materials competitive not only with the nylons but also with metals and ceramics [Mark *et al.*, 1988a; Brydson, 1995b; Sabel *et al.*, 1996]. With the excellent properties, POM is widely use in many areas, such as automotive, hardware, industrial, agricultural, plumbing and consumer products [Sinker, 1990]. However, an inferior impact resistance and extremely notch sensitive compared to that of other engineering plastics limits its applications. As other crystalline polymers, POM is rigid, brittle and chemically unreactive. POM shows outstanding resistance to organic solvents without stress cracking. POM is relatively impervious to neutral inorganic and organic chemicals including aliphatic and aromatic hydrocarbons, due to their highly crystalline nature [Brydson, 1995b].

PETG offered the best balance of properties such as high toughness, good melt strength and high glossiness. Amorphous copolyesters are resistant to whitening from internal crazing when physically stressed. However, PETG has poor solvent and chemical resistance. Since it is an amorphous material, PETG offers a range of processing parameter broader than that of normal crystallizable polymers.

The polymer blending can provide materials that possess unusual combination of properties. For instance, when amorphous and crystalline polymers are blended, due to their complementary properties, particularly varied combinations of the properties can be achieved [Erro *et al.*, 1996]. POM and PETG blending was attempted to achieve improvement in mechanical and chemical properties, where PETG contribute fracture toughness properties and reduce the shrinkage rate of POM after molding,

while POM ensures good chemical resistant, stiffness and strength. In general, polymer blend morphologies can be divided into two types, dispersed phase/droplet and co-continuous type [Yuan & Favis, 2004]. There is less than 100 papers have been devoted to study the blends with co-continuous morphologies. The co-continuous blends have recently become the subject of intense study because one of the interesting features of these morphologies is that both the component, in all directions, can fully contribute to the properties of blends [Veenstra *et al.*, 1999b; Riscanu *et al.*, 2004]. There are some literatures showing increases in impact strength in the case of co-continuous blends. Mamat *et al* [1997] investigated the impact properties nylon-6/acrylonitrile-butadiene-styrene (ABS) blend. It was found that the co-continuous nylon-6/ABS blend exhibited higher impact strength than other blend composition. It maybe expected that the fracture toughness of PETG/POM blend could be enhanced in the presence of co-continuous morphologies.

POM is known to be difficult to compatibilize with other polymers due to the simplicity of its chains [Utracki, 1990]. Thus, it could be expected that the mechanical properties of the PETG/POM blend could be further enhanced via the incorporation of a suitable compatibilizer. TPU is a linear segmented block copolymer [Lu & Macosko, 2004] was chosen because it has been found suitable to compatibilize the POM. The amine group in the TPU is expected to form hydrogen bonding with POM and this will increase the compatibility between PETG and POM [Utracki, 1990].

1.3 Research Objective

This study is concerned with PETG/POM blend. The primary objectives of these studies are divided into the following categories:

- To explore the effect of blend compositions on the thermal, mechanical and morphologies properties of PETG/POM blends.
- To identify the composition range, which co-continuity can occurs in PETG/POM blend.
- To identify suitable compatibilizer for PETG and POM, in order to further enhance the compatibility between the components, and synergize the mechanical properties.
- To study the effect of testing speed on the mechanical and morphology behavior of co-continuous PETG/POM blends.

CHAPTER 2 LITERATURE REVIEW

2.1 Thermoplastics

Thermoplastics are resins that repeatedly soften when heated and harden when cooled. Many are soluble in specific solvents and burn to some degree. Compared with thermosets, thermoplastics generally offer higher impact strength, easier processing and better adaptability to complex designs [Rosato, 1997]. The thermoplastic can be divided into two classes, commodity plastics (i.e. polyethylene (PE), polypropylene (PP), and polystyrene (PS)) and engineering plastics (i.e. polyoxymethylene (POM), polyamide (PA) and polycarbonate (PC)).

2.2 Polyoxymethylene

Polyoxymethylene or polyacetal became commercially available early 1960. POM has a good potential to replace metal because of its unique properties [Akin, 1962; Barker & Price, 1970; Sabel *et al.*, 1996]. POM resins are crystalline polymers with a degree of crystallinity ranging from 58 to 77%. [Mark *et al.*, 1988a; Forschirm & McAndrew, 1996] The POM has a good balance in their strength, stiffness and toughness. Besides that, POM performs remarkably well in applications where metals were historically used. The ability to predict the long term strength, toughness, creep, fatigue, chemical resistance, dimensional stability and wear resistance of POM in known environments of temperature, pressure and atmosphere allows engineers the freedom to design parts, which is lower in cost than metals in the final form [Sinker, 1990; Brydson, 1995b]

POM comprises homo- and copolymers of aldehydes and cyclic acetals whose characteristic building blocks $-\text{CHR}-\text{O}-$ are arranged into essentially linear chains of alternating carbon and oxygen atoms. POM has a recurring unit of oxymethylene, $(-\text{CH}_2-$

O—). The homopolymeric POM can be obtained via polymerization of formaldehyde or cyclic oligomers such as trioxane or tetroxane. This is shown in Figure 2.1. The Hemiacetalic or hydroxyl end groups originate through transfer reactions of the polymerizing chains with water. If another polymerizable monomer or prepolymer having an acetal structure is present during the polymerization of formaldehyde or trioxane then it will be built into polymer chain according to its copolymerization parameter [Sabel *et al.*, 1996]. This is shown in Figure 2.2.

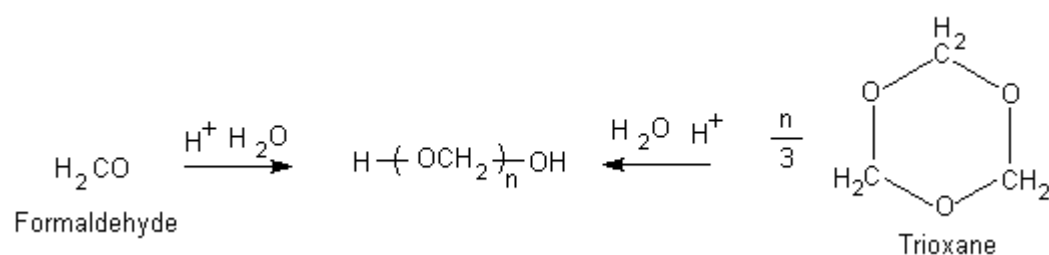


Figure 2.1: Polymerization of formaldehyde and trioxane to homo-polyoxymethylene. [Sabel *et al.*, 1996]

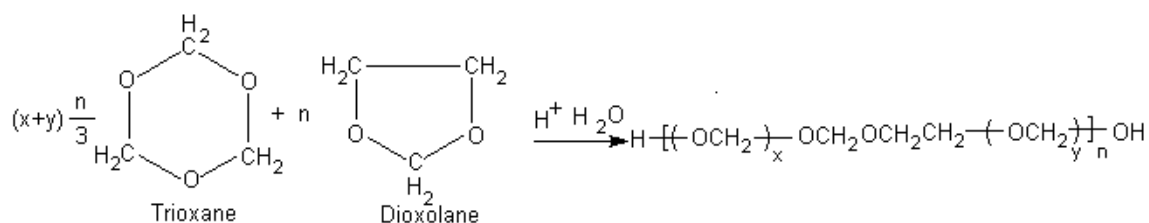


Figure 2.2: Polymerization of polyoxymethylene copolymer. [Sabel *et al.*, 1996]

In addition, POM is available in a broad range of molecular weights to meet the needs of the various plastics processing techniques [Salamone, 1996]. POM can be readily injection molded into parts that request no post processing, such as machining, deburring, riveting, welding or painting. POM can also be pigmented to any opaque color. POM is extremely resistant to a wide range of solvents and is not hygroscopic. They remain dimensionally stable in harsh environments. However, POM is prone to attack by strong acids and strong oxidizing agents such as hypochlorite and is not recommended for use in these environments [Sinker, 1990]. POM is generally

equivalent to nylons in their fatigue endurance, creep resistance, stiffness and water resistance but nylons are superior in impact toughness and abrasion resistance. [Brydson, 1995b]

2.3 Amorphous copolyester

Poly (ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate) (PETG) is an amorphous thermoplastic copolyester. The “G” in the designation of PETG copolyester indicates a second glycol, 1,4-cyclohexanedimethanol, incorporated in the polymer. Figure 2.3 shows the repeating unit of the PETG. In contrast to the semicrystalline homopolyester poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET), the PETG did not undergo crystallization on heating or on plasticization by the dissolved species. This is due to the comonomer, cyclohexanedimethanol is responsible for the completely amorphous nature of this polymer [Yu *et al*, 2002; Yu *et al*, 2003]. Amorphous copolyesters are transparent, even as thick parts, high toughness, low shrinkage and high stability in dimension. Moreover, the PETG offers a range of processing parameters broader than that of normal crystallizable polymers [Binsack, 1996; Yu *et al.*, 2002]. In order to increase the glass transition temperature and thermostability, chain flexibility must be decreased. This can be accomplished, for example by increasing the aromatic part of the dicarboxylic acid, by stiffening cycloaliphatic diols, by increasing the intermolecular forces with polar groups or by special heterocyclic diols [Binsack, 1996].

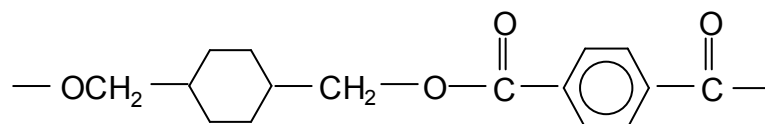


Figure 2.3: Repeating unit of PETG [Papadopoulou & Kalfoglou, 1997b]

2.4 Polymer blends

Many plastics manufacturer and compounders are developing new blended products because they offer a convenient, less expensive alternative to developing a new product [Mark *et al.*, 1988b]. Polymer blends are a mixture of at least two polymers or copolymers [Utracki, 1990]. Polymer blending is one of the effective ways to obtain materials with specific properties. Blending not only can improve mechanical properties, chemical properties, processibility but also the desire properties. Blending of high performance engineering plastics with a low cost polymer to develop a material with properties meeting the specification of customer. Moreover, polymer blending can form a high performance blend from synergistically interacting polymer. In recycling industry, blending with scrap plastics has high economy value and also reduces the environmental problem. According to Syed Jamaludin [2003], two or more polymers may be blended together to form a wide variety of random or structured morphologies to obtain products that potentially offer desirable combinations of characteristics. Figure 2.4 shows the general relation of the polymer and copolymer blends.

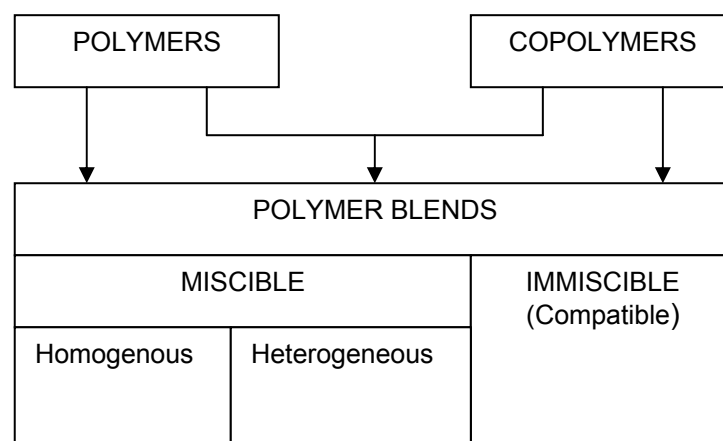


Figure 2.4: Interrelations in polymer blend nomenclature. [Utracki, 1990]

Properties of the polymer blends are dependent on the miscibility of the blends. For the miscible polymer blends, the properties may be intermediate between those of the individual components. In this case we called additive behavior [Fried, 1995]. In

other cases, properties of the polymer blends may exhibit either positive or negative deviation from additivity as shown at Figure 2.5.

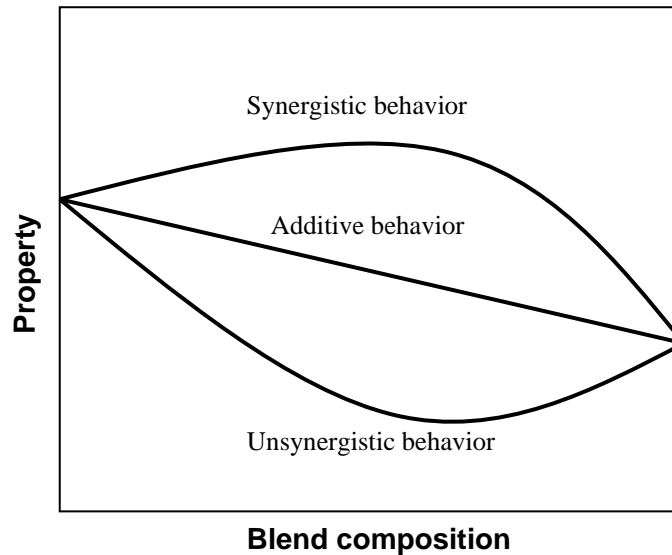


Figure 2.5: Compounding aims for synergistic effect [Rosato, 1997]

2.5 Factors in miscibility and immiscibility

The miscibility and immiscibility of polymer blends are dependent to on several factors [Utracki, 1990]. There are:

(a) Polarity

Polymers with a similar structure or similar polarity are less likely to repel each other, whereas more likely to form miscible blends [Gaylord, 1976; Paul, 1978]. Diverging polarities usually produce immiscibility.

(b) Specific Group Attraction

Polymer that are drawn to each other by hydrogen bonding, acid-base, charge transfer, ion-dipole and donor-acceptor adducts. When these attractions occur they are tends to produce miscibility [Deanin & Manion, 1999].

(c) Molecular Weight

Normally, lower molecular weight permits greater randomization on mixing and therefore greater gain of entropy, which favors miscibility [Markham, 1991]. The polymers with similar molecular weights are more miscible, whereas polymers with different molecular weights may be immiscible, even if they both have the same composition.

(d) Ratio

Two polymers appear immiscible when high amounts of both components. However, it is possible that a small amount of one polymer may be soluble in a large amount of the other polymer, as understood in conventional phase rules. This consideration is very important in natural compatibility [Bonner & Hope, 1993].

(e) Crystallinity

In a polymer blend, when a polymer crystallizes, this adds another phase to the system. When both polymers in a blend crystallize, this will usually form two separate crystalline phases. It is quite rare for the two polymers to cocrystallize in a single crystalline phase [Chen & White, 1993].

2.6 Compatibilization in polymer blends

Polymer blending is convenient route for the development of new polymeric materials, which combine the excellent properties of more than one existing polymer. Besides that, blends can be tailored to meet the requirements of specific applications. They can be developed much more quickly than new polymers and require much less capital investment. The properties of the blends are strongly depending on the compatibility of the system. However, most of the polymer blends are found to be incompatible. These incompatible blends are characterized by a two-phase morphology, narrow interphase, poor physical and chemical interactions across the phase boundaries and poor mechanical properties [George *et al.*, 1995]. These

problems can be alleviated by the addition third component into the incompatible polymer blends to enhance the degree of compatibility between the constituent component [Bonner & Hope, 1993]. The third component is called compatibilizer. Compatibilizers are macromolecular species exhibiting interfacial activities in heterogeneous polymer blends. Usually the chains of a compatibilizer have a blocky structure, with one constitutive block miscible with one blend component and a second block miscible with the other blend component [Koning *et al.*, 1998]. Many authors are using the term *miscible* and *compatible* casually and indiscriminately. Therefore, many of the literature are ambiguous or confusing. Generally, the term *miscible* will be used to describe polymer blends that have theoretical thermodynamic miscibility down to the segmental level. The term *compatible* will be used to describe polymer blends that have useful practical properties, regardless of whether they are theoretically miscible or immiscible [Deanin & Manion, 1999].

The mechanical properties of a blend will be determined not only by the properties of its components, but also by the phase morphology and the interphase adhesion. The phase morphology and the interphase adhesion are important from the viewpoint of stress transfer [Bonner & Hope, 1993]. From a theoretical perspective, much can be learned about the nature of the compatibility and the expected properties of the blend by probing its morphology. Figure 2.6(a) shows a miscible polymer blend consists of a single phase. On the molecular level, the polymer A molecules is intermingle with polymer B. In addition, the miscible polymer blend has only one phase, it is much like a random copolymer in properties and processing. In order to be miscible, some attraction between the two polymers must present to partially overcome the intramolecular cohesive forces of the individual polymer. Interpolymer attractions are due to the specific interactions between functional groups on polymer A with different functional groups on polymer B. However, only few polymer blends are totally miscible [Mark *et al.*, 1988b].

Polymer A forms a separate phase from polymer B, as shown in Figure 2.6(b). This is a second possible morphology for polymer blend, immiscible blend. Immiscible blend is more common than one phase miscible blend. Generally, the polymer with lower concentration form a discontinuous or discrete phase, however the polymer with high concentration forms a continuous phase. The polymer blends are neither totally miscible nor totally immiscible, are called partially miscible. Partially miscible polymers may form completely miscible blends when each polymer is present in small amounts. However, as the ratios progress toward equality, the phases separate. Partially miscible blends are consisting of two phases, the phases may not have a well-defined boundary. Figure 2.6(c) shown that polymer A molecules can significantly penetrate into the polymer B phase and *vice versa*. The molecular mixing that occurs at the interface of a partially miscible two phases blend can stabilize the domains and improve interfacial adhesion, which explains why these two phase blends usually have good bulk properties [Mark *et al.*, 1988b].

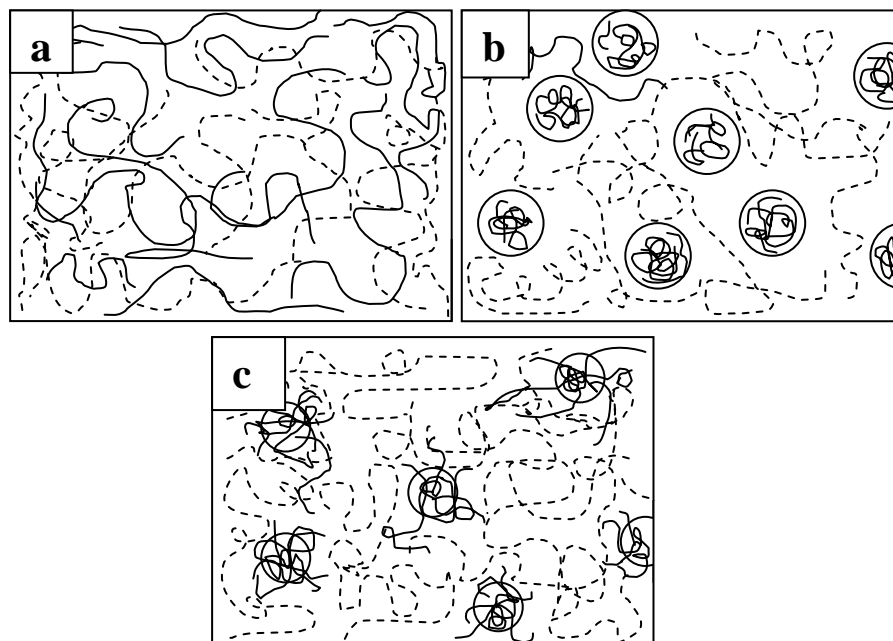


Figure 2.6: Morphologies of a blend of polymer A (Solid lines) and polymer B (dashed lines): (a) miscible, (b) immiscible, (c) partially miscible. [Mark *et al.*, 1988b].

2.6.1 Addition of block and grafted copolymer

The emulsification of polymer blends has been proposed as the most efficient tool for obtaining a fine phase morphology and good mechanical properties. The best way to validate that concept is to tailor block and grafted copolymers and to investigate the beneficial effects that they can have on immiscible polymer blends. During last decade, a large number of studies have reported that the addition of block or grafted copolymers is one of an effective way to compatibilize the immiscible blends [Duvall *et al.*, 1994; Jeon *et al.*, 2004]. However, block copolymers have been more frequently investigated than grafted copolymer. The block and grafted copolymers containing segments chemically identical to the blend components are obvious choices as compatibilizer, given that miscibility between the copolymers segments and the corresponding blend components is assured. Figure 2.7 shows how the block and grafted copolymer can penetrate both phases of an immiscible blend when mixed. A segment (white dot) and B segment (black dot) either block or grafted copolymers are identical to polymer A and polymer B. The working hypothesis is that segment A penetrates polymer A and segment B penetrates polymer B. The interfacial adhesion of the blend is improved due to the compatibilizer segments, which reside in separate phase, are linked covalently [Mark *et al.*, 1988b; Koning *et al.*, 1998].

The efficiency of the compatibilization is influenced by the molecular weights of the segments in the block or grafted copolymers. When the molecular weight of the compatibilizer segments is low, the depth of penetration into the domains by the compatibilizer is also low. This leads to the poor interfacial adhesion. The penetration may be high when the molecular weight of the compatibilizer segments is very high [Paul & Newman, 1978]. For example, Macaúbas & Demarquette [2001] added styrene–butadiene–styrene (SBS) and styrene–ethylene/butylene–styrene (SEBS) triblock copolymers as compatibilizers in polypropylene/polystyrene system. The addition of compatibilizers to the PS phase resulted in a reduction of interfacial tension

following an emulsion curve. It was shown that for both compatibilizers the concentration at which the interfacial tension essentially levels off is smaller than the concentration at which the average radius of the dispersed phase essentially levels off. The morphological, viscosity and interfacial tension results showed that SEBS is a better compatibilizer for the PP/PS blend than is SBS. Chen *et al* [2002] have investigated the compatibilization effect of triblock copolymers of poly[styrene-*b*-(ethylene-co-butylene)-*b*-styrene] and the diblock copolymer of poly[styrene-*b*-(ethylene-co-butylene)] in high density polyethylene/synodiotactic polystyrene (sPS) blends. Morphology observation showed that phase size of the dispersed sPS particles was significantly reduced on addition of the copolymers and the interfacial adhesion between the two phases was dramatically enhanced. Tensile strength of the blends increased at lower copolymer content but decreased with increasing copolymer content. The elongation at break of the blends improved and sharply increased with increments of the copolymers. Papke and Karger-Kocsis [2001] have studied the compatibilizing effect of ethylene/propylene rubber grafted with glycidyl methacrylate (EPR-g-GMA) in the thermoplastics elastomers/ poly(ethylene terephthalate) blends. It was found that the blend compatibility with PET is strongly improved when the EPR-g-GMA is used as compatibilizer in the blends. Table 2.1 lists various compatibilized systems that have been studied.

2.6.2 Addition of functional polymers

There are many published research papers relating to the addition of functional polymers as compatibilizers. Basically, a polymer chemically identical to one of the blend components is modified to contain functional or reactive units [Bonner & Hope, 1993]. These functional units have some affinity for the second blend component, which have the ability to chemically react with the second blend component. However, there have other types of interaction such as ionic are also possible. The functional modification may be achieved in a reactor or via an extrusion modification process.

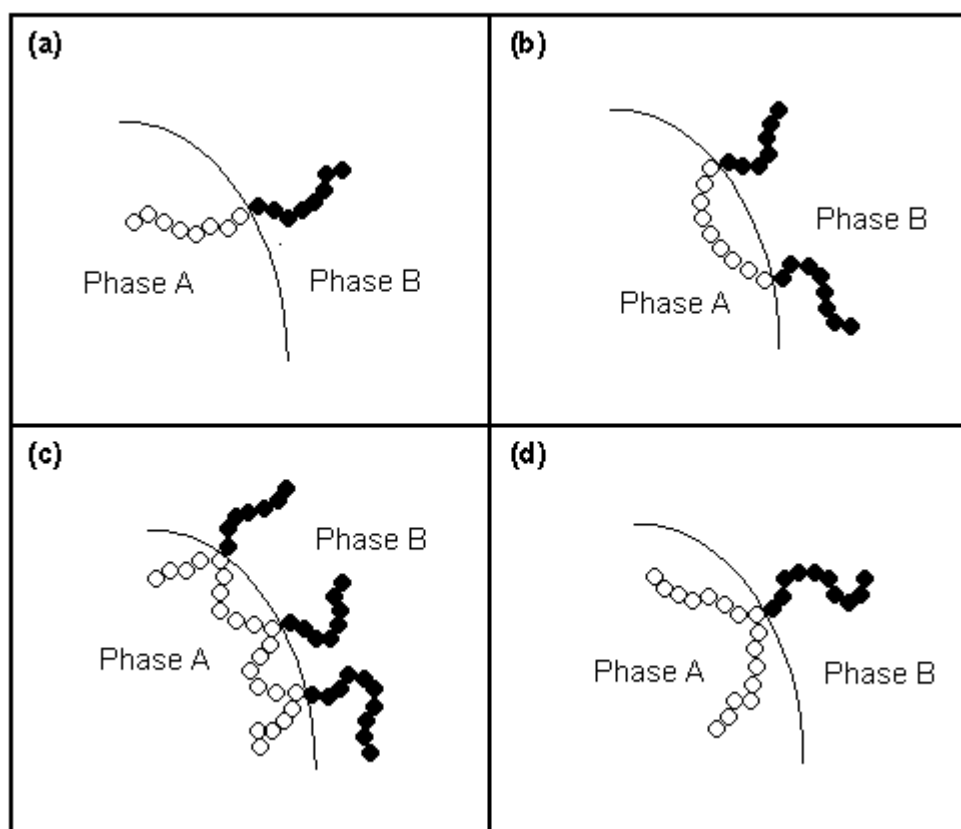


Figure 2.7. Penetration of block or grafted-copolymer compatibilizers into the A and B phase of a heterogeneous polymer blend: (a) diblock; (b) triblock; (c) multigraft and (d) singlegraft. [Koning *et al.*, 1998]

Table 2.1 Compatibility by premade copolymers (Koning *et al.*, 1998)

Type of blend	Major component	Minor component	Compatibilizer
A/BA–B block	PE or PS	PS or PE	HPB-b-PS, SEBS, SBS
	PBT or PS	PBT or PS	PS-b-PBT or PS-b-PET
A/B/A–C block	PPO or PBT	PPO or PBT	PS-b-PET or PS-b-PBT
	PS or PC	PC or PS	PS-b-PCL
A/B/C–D block	Phenoxy	PPO	PS-b-PMMA
	PPO	SAN	PS-b-PMMA
A/B/A–B graft	EPDM	PMMA	EPDM-g-MMA
	PBT	PS	PBT-g-PS

Note: PPO = poly(2,6-dimethyl-1,4-phenylene oxide)
EPDM-g-MMA = ethylene-propylene-diene elastomer grafted with methyl methacrylate
PMMA = Poly(methyl methacrylate)

Functionalised polymers (usually maleic anhydride or acrylic acid grafted polyolefins) are commercially available at acceptable cost to be used as compatibilizers. For example, the grafting of maleic anhydride or similar compounds to polyolefins, result in the formation of pendant carboxyl group which have the ability to form a chemical bridge with polyamides via their terminal amino groups [Bonner & Hope, 1993]. Papadopoulou and Kalfoglou [2000] have studied the efficiency of maleic anhydride modified polyolefins on the PET/PP blend. Recently, Aravind *et al* [2004] have studied the compatibilizing effect of maleic anhydride grafted ethylene propylene rubber (EPM-g-MA) in ethylene propylene diene rubber/ Poly(trimethylene terephthalate) (PPT) blends. It was found that the addition of EPM-g-MA reduces the domain size of the dispersed phase followed by a leveling off at higher concentrations of the compatibilizer. The addition of EPM-g-MA to the blends tends to decrease the free volume showing its compatibilizing effect. Table 2.2 lists the polymer blends with addition of functional polymer.

Table 2.2: Example of polymer blends with functional polymer

Major component	Minor component	Compatibilizer	References
PPT	EPDM	EPM-g-MA	Aravind <i>et al.</i> , 2004
iPP or PA66	PA66 or iPP	IPP-g-MA	Sacchi <i>et al.</i> , 2004
LDPE	PA	PE-g-MA	Jiang <i>et al.</i> , 2003
PSF	TLCP	PSF-g-MA	Zhang & He, 2002
PP	PA	PP-g-MA	Tseng <i>et al.</i> , 2001
		PP-g-MA-co-POP	

2.6.3 Reactive blending

Addition block or grafted copolymer presents the best technical option for compatibilization. This is because of the effectiveness in reducing the interfacial tension and in improving the interfacial adhesion by making entanglements or bridging different polymer chains near the interface. However, these types of materials suffer a number of disadvantages; they are expensive, not commercially available and need to be tailor made for a particular blend. On the other hand, most of the block copolymers are in microphase separated state at mixing temperature, they are very high viscosities making it very hard to disperse them near the interface between two phases [Kim *et al.*, 1997]. A new technical method of producing compatible polymers blends is called reactive blending. This method relies on the in situ formation of copolymers or interacting polymers. The in situ compatibilization is different with other compatibilization routes in that the blend components themselves are either chosen or modified so that the reaction occurs during melt mixing. Thus no addition of a separate compatibilizer is needed [Bonner & Hope, 1993]. In some cases, the reaction may be produced by adding a monomeric ingredient, which can serve as a catalyst, free radical initiator and coreactant in the reaction between the two polymers [Deanin & Manion, 1999]. For example, Samios *et al* [2000] have investigated the in situ compatibilization of polyurethane (PU) with PET. The mechanical and thermal properties indicated good blend compatibility typical of a polymeric alloy. Morphology examination revealed good dispersion and strong interface adhesion of the PET/ thermoplastic polyurethane (TPU) blends. The effect was dependent on the treatment conditions. The reactive compatibilization of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and PBT was reported by Aert *et al* [2001]. PPE/PBT blends are incompatible, and the phase morphologies obtained during blending of these polymers. When PPE is functionalized selectively, in situ compatibilization during processing is feasible. Due to the formation of segmented copolymers, which act as compatibilizing agents, stabilization of the morphology obtained during blending. Oh *et al* [2003] have reported the preparation of

in situ compatibilization PP/natural rubber (NR) blends via twin-screw extruder and ultrasonically treated during the extrusion process. The improved interfacial adhesion, morphology and mechanical properties of the blends are believed to be due to the formation of in situ copolymer at the interface of two immiscible polymers caused by an ultrasonic treatment without the use of any chemicals. Recently, the blends of isotactic polypropylene (iPP) and uncured ethylene–propylene diene rubber (EPDM) treated by high power ultrasonic waves during extrusion have been investigated by Feng and Isayev [2004]. The yield strength, elongation at break, tensile strength, and toughness of ultrasonically treated PP/EPDM blends were improved at certain conditions of ultrasonic treatment compared to those of untreated blends.

2.7 Polyoxymethylene blends

Numerous researchers have described the investigation on the polyoxymethylene blends. The blends of polyoxymethylene with polyurethane [Chiang & Huang, 1988; Chiang & Huang, 1989; Palanivelu *et al.*, 2000; Mehrabzadeh & Rezaie, 2002], polypropylene [Brydson, 1995a; Utracki, 1998; Huang *et al.*, 2003], polycarbonate [Utracki, 1998; Chang *et al.*, 1991], phenoxy [Erro *et al.*, 1996], ethylene-propylene-diene terpolymer [Chiang & Huang, 1993], poly(vinyl phenol) [Machado & French, 1992] have been reported.

2.7.1 Polyoxymethylene/polyurethane blends

POM has good mechanical properties and good resistance to crack initiation, whereas it is notch sensitive and poor resistance to crack propagation [Chiang & Huang, 1989]. The impact strength and toughness of POM can be improved by incorporation of dispersed rubber phase by reactive blending. The rubber particles dispersed in the rigid matrix may stop the craze growth, which can lead to the formation of failure cracks during impact. Furthermore, the rubber particles may act as a stress concentrator and forming a barrier to the extension of crazing [Mehrabzadeh & Rezaie,

2002]. POM toughened by TPU has been reported in many literatures [Chiang & Huang, 1988, Chiang & Huang, 1989, Palanivelu *et al.*, 2000, Mehrabzadeh & Rezaie, 2002].

Chiang *et al* [1988; 1989] have investigated the mechanical, physical, thermal and dynamic mechanical properties, morphology and compatibility of POM/TPU blends. The ester based and ether based thermoplastic polyurethane were selected to blend with POM. It was reported that the tensile strength, modulus, density and crystallinity decreased by increasing the TPU concentration. The elongation of blends reaches a maximum at 20wt% of TPU. The notched Izod impact strength of blend showed an improvement and reached a maximum at 10wt%. The ether based TPU showed better result than the ester based TPU. From the dynamic mechanical analysis results, when the TPU concentration increased, the height of the damping peak also increased. However, there is no transition temperature shift. The SEM micrographs showed that the blends exhibit a continuous morphology with domain size varying from 4 to 10 μ m for TPU. However, at a concentration of 50wt% of TPU, the dispersed TPU particles tend to aggregate.

Palanivelu and coworker [2000] focused on the investigation of the mechanical, morphological and rheological properties of POM/TPU blends. Four different blending ratio were selected, i.e. 90/10, 80/20, 70/30 and 60/40wt%. The tensile and flexural strength of the blends decreased with the increasing of TPU concentration. However, the notched impact strength increased with increasing of TPU concentration in blends. Based on the SEM investigation, the impact fractured surfaces shown droplet dispersion morphology. The melt flow curves of the POM/TPU showed lower melt viscosity than those of feedstocks in the major range of experimental shear rates.

Mehrabzadeh and Rezaie [2002] have studied the impact modification of POM with ester based TPU and applied diphenylmethane diisocyanate (MDI) as modifier. The mechanical properties, thermal behavior and morphology of POM/TPU blends consisting of 5~50wt% of TPU were investigated. The maximum impact strength was achieved at POM/TPU 85/15 with 3phr of MDI. The later served as crosslinking agent and a compatibilizer. SEM micrographs of the fractured surfaces showed that the two phase morphology of the blends and that the TPU was dispersed in POM as a matrix phase.

2.7.2 Polyoxymethylene/polypropylene blends

An immiscible blend of POM with semicrystalline PP has been reported, [Utracki, 1998]. As in other immiscible blends, a compatibilizer is needed to compatibilize the blends. PP/POM blends are usually compatibilized by addition of acidified or expoxidified polyalkenes, since POM can develop strong hydrogen bonding with acidic or epoxy groups [Utracki, 1998]. PP exhibits better flexibility and higher impact strength, but has relatively lower tensile strength and deflection temperature. Thus, blends of PP and POM may provide better impact resistance for POM and better flexural modulus for PP, combined with lower cost, compared with POM [Brydson, 1995a].

Huang *et al* [2003] compatibilized the PP/POM blends with ethylene vinyl alcohol (EVOH) copolymers. The ethylene group in the EVOH is partially miscible with PP, whereas the hydroxyl group in the EVOH can form hydrogen bonding with POM. The EVOH tends to reside along the interface and act as a surfactant to reduce the interfacial tension and increase the interfacial adhesion between PP and POM in blends. The addition of EVOH copolymer with 56wt% of vinyl alcohol in the blend disturbs the crystallization of PP and POM and resulted in a decrease in the crystallinity of the blend. The melt flow rate (MFR) of the uncompatibilizer blends showed higher

MFR value than the compatibilized blends. The impact strength of the PP/POM blends increased with increasing of PP concentration in blend. However, the tensile strength and the tensile modulus reduced with the increasing of PP concentration.

2.7.3 Polyoxymethylene/polycarbonate blends

The PC and POM blends are immiscible and both resins require toughening. The addition of crystalline POM to the amorphous PC is to improve the solvent and chemical resistance [Utracki, 1998]. Chang *et al* [1991] investigated the morphology, mechanical and thermal properties of the immiscible PC/POM blends. The formation of a strong interpenetrating interface in PC/POM blends significantly increased the tensile yield strength, modulus and heat distortion temperature above the average values for the pure materials. The addition of TPU into the PC/POM blends does not improve the toughness of the blend. This is because of the elastomer distributes selectively in the PC phase.

2.7.4 Polyoxymethylene/phenoxy blends

When a crystalline polymer was blended with an amorphous polymer, due to their usually complementary properties, varied combinations of properties can be achieved. The poly(hydroxy ether of bisphenol-A) (phenoxy) is a fully amorphous polymer that gives rise to a number of miscible blends with other polymer. The transitions and mechanical properties of POM/phenoxy blends were studied by Erro *et al* [1996]. The POM/phenoxy blends are composed of two almost pure phases. Although the POM/phenoxy blends are fully immiscible they showed synergisms in the modulus of elasticity and mainly in ductility at phenoxy rich compositions. As expected the density and crystallinity of the blends decreased with the increasing of phenoxy concentration.

2.7.5 Polyoxymethylene/ethylene-propylene-diene terpolymer blends

Chiang and Huang [1993] investigated the properties of POM and EPDM blends. The addition of EPDM into the POM matrix is to increase the toughness and elongation at break of POM. The major differences between the behaviors of the POM and EPDM are the higher value of Young modulus and tensile strength for POM and the higher values of elongation at break point and higher impact strength for EPDM. Tensile strength and tensile modulus showed negative deviations on the blend, as expected. It is known that the tensile strength of a toughened plastic decreases with the rubber content, while the elongation at break increases [Chiang & Huang, 1999]. The impact strength of the POM/EPDM blends increased with the increasing of EPDM. The EPDM being a soft rubbery phase has improved the impact resistance by inducing crazing of POM and absorbing more energy during impact fracture.

2.7.6 Polyoxymethylene/poly(vinyl phenol) blends

Machado and French [1992] focused on the investigation of the dynamic mechanical behavior, melting behavior, density and morphology of POM/poly (vinyl phenol) blends. POM/poly(vinyl phenol) blend system shows a single glass transition temperature, which indicates the miscibility of POM/ poly(vinyl phenol) blends. Analysis of the melting point depression yielded an approximate interaction parameter, which was in excellent agreement with that obtained from the calorimetric mixing of chemical analogs. The observation of a significant negative volume of mixing supported the miscibility.